Bioresource Technology 169 (2014) 367–373

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Thermogravimetric analysis and fast pyrolysis of *Milkweed*

Seung-Soo Kim [a], Foster A. Agblevor [b,*]

[a] Department of Chemical Engineering, Kangwon National University, 346 Joongang-ro, Samcheok, Gangwon-do 245-711, Republic of Korea
[b] Department of Biological Engineering, Utah State University, Logan, UT 84322-4105, USA

HIGHLIGHTS

- Thermogravimetric analysis of *Milkweed* in TGA.
- Fast pyrolysis of *Milkweed* in a bubbling fluidized bed reactor.
- Milkweed pyolysis oil hve muchiger HHV compared to othr lgnocelluosic pyrolyis oils.
- The pH of te Mikweed pyrlysis oils was almost neutral (pH 7.37) which was the higest reported data.

ARTICLE INFO

Article history:
Received 8 April 2014
Received in revised form 20 June 2014
Accepted 23 June 2014
Available online 9 July 2014

Keywords:
Fast pyrolysis
Herbaceous biomass
Milkweed
Bio-oil
Bubbling fluidized bed reactor

ABSTRACT

Pyrolysis of *Milkweed* was carried out in a thermogravimetric analyzer and a bubbling fluidized bed reactor. Total liquid yield of *Milkweed* pyrolysis was between 40.74% and 44.19 wt% between 425 °C and 550 °C. The gas yield increased from 27.90 wt% to 33.33 wt% with increasing reaction temperature. The higher heating values (HHV) of the *Milkweed* bio-oil were relatively high (30.33–32.87 MJ/kg) and varied with reaction temperature, feeding rate and fluidization velocity. The selectivity for CO_2 was highest within non-condensable gases, and the molar ratio of CO_2/CO was about 3 at the different reaction conditions. The ^{13}C NMR analysis, of the bio-oil showed that the relative concentration carboxylic group and its derivatives was higher at 425 °C than 475 °C, which resulted in slightly higher oxygen content in bio-oil. The pH of aqueous phase obtained at 475 °C was 7.37 which is the highest reported for any lignocellulosic biomass pyrolysis oils.

1. Introduction

Biomass resources such as woody biomass (Agblevor et al., 1995, 2010; Bridgwater, 2012; Yathavan and Agblevor, 2013; Kim et al., 2014), herbaceous plants (Gu et al., 1992; Boateng et al., 2010; Choi et al., 2011), aquatic plants (Kim et al., 2013; Sanchez-Silva et al., 2012), and poultry litter (Kim et al., 2009; Mante and Agblevor, 2010), are being investigated as potential resources for fuels and chemicals. Lignocellulosic biomass, which is composed of hemicellulose, cellulose, lignin and minor amounts of other organics, is recognized as a major source of renewable energy (Bridgwater et al., 1999). Herbaceous plants such as *Pennycress* (Boateng et al., 2010), *Milkweed* (Foster and Karpiscak, 1983; Gu et al., 1992), and hemp (Choi et al., 2011) are being considered as potential energy corps because they are fast growing and short rotation crops. *Milkweed* contains about 1–2% latex, and was investigated as a source of natural rubber in Germany and the United States during World War II. No record has been found of large-scale success. *Milkweed* is now being grown commercially for production of floss for use as hypoallergenic fillers in pillows and comforters (Evangelista, 2007). Foster and Karpiscak (1983) investigated the use of arid land plants for direct combustion, production of liquid fuels, and feedstocks for hydrocarbon production. *Milkweed* grows in Nevada, New Mexico, Arizona, and coastal range of California. The Plant Resource Institute, Salt Lake City, Utah projects 17.9 t/ha yr (dry basis) were possible with three cuttings. They reported that *Milkweed* could also yield 20% liquid hydrocarbons (dry basis) with heating values up to 34.9 MJ/kg. Gu et al. (1992) investigated the correlation between chemical composition of *Milkweed* and its thermal decomposition. They analyzed FT-IR spectra for the pyrolysis of *Milkweed* at 300 °C, and reported that acetic acid, formic acid and methanol were formed in addition to CO_2 and H_2O.

Fast pyrolysis studies have been widely used for converting waste biomass and lignocellulosic biomass into liquid and gaseous products and solid char residue. Mullen et al. (2013) researched hydrotreating of fast pyrolysis oils from protein-rich pennycress seed presscake, and studied the mild batch hydrogenation of the

* Corresponding author. Tel.: +82 33 570 6544; fax: +82 33 570 6535 (S.-S. Kim). Tel.: +1 435 797 9268; fax: +1 435 797 1248 (F.A. Agblevor).

E-mail addresses: sskim2008@kangwon.ac.kr (S.-S. Kim), foster.agblevor@usu.edu (F.A. Agblevor).

http://dx.doi.org/10.1016/j.biortech.2014.06.079
0960-8524/

pyrolysis oil at ~13.8 MPa H_2 and 320 °C over precious metal catalyst supported on charcoal: Ru/C, Pd/C and Pt/C. The upgraded pyrolysis oil contained <15 wt% total hetero atom content (O + N + S) with an HHV of 33.4–37.0 MJ/kg, and they reported that the products were very rich in long chain aliphatic hydrocarbons. Yathavan and Agblevor (2013) researched catalytic pyrolysis of *Pinyon-Juniper* in a bubbling fluidized bed reactor using red mud and HZSM-5 as a catalyst. The higher heating value (HHV) of the red mud catalyzed bio-oil was 29.46 MJ/kg, and that catalyzed by HZSM-5 was 28.55 MJ/kg.

In this work, thermogravimetric characteristic and kinetic of *Milkweed* was investigated using TGA, and fast pyrolysis characteristics of *Milkweed* in a bubbling fluidized bed reactor were also investigated. The overall goal of this study is to develop *Milkweed* as a high energy density feedstock for biofuel production.

2. Experiment

Milkweed (*Asclepias syriaca*) was obtained from the University of Western Illinois, Alternative Crops Research Program. It was ground in a Wiley mill (Thomas Scientific, Model 4) to pass 2 mm screen. The moisture content was determined using a Denver Instruments IR 60 infrared moisture analyzer (Denver Instruments, Bohemia, NY), and ash content of experimental sample were determined using ASTM E1755 (Annual book of ASTM standards, 2000). The volatile matter, fixed carbon, and thermogravimetric analysis were determined using TA Q500 thermogravimetric analyzer (TA Instruments, New Castle DE). The elemental compositions were determined using Flash 2000 organic elemental analyzer (Thermo Fisher Scientific. Inc., Waltham, MA). The higher heating value (HHV) of *Milkweed* was determined using IKA basic bomb calorimeter (IKA Works Inc., Wilmington, NC).

A sample mass of 15 ± 1 mg, was used for the thermogravimetric analysis, in a Nitrogen atmosphere at a gas flow rate of 40 ml/min. The particle size of *Milkweed* was <2 mm for TG analysis. The heating rates were set at 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min and the samples were heated from 20 °C to 700 °C.

The fast pyrolysis of *Milkweed* was conducted in a bubbling fluidized bed reactor. The schematic diagram of experimental equipment is shown in Fig. 1. The reactor consisted of a 5.08 cm schedule stainless steel pipe, 50.8 cm high (including 14.0 cm pre-heater zone below the gas distribution plate) and equipped with a 100 μm porous metal gas distributor. The bed material was silica sand (60–80 mesh) which was fluidized with nitrogen. The diameters of bed material was between 177 μm and 231 μm. The reactor tube, which contained a bubbling fluid bed with back mixing of the feed, was externally heated with three zone electric furnace (Thermcraft Inc., Salem, NC).

The ground *Milkweed* samples (<2 mm) were loaded into a feed hopper (batch-wise) and conveyed by a twin-screw feeder into an entrainment compartment where high-velocity nitrogen gas entrained the feed and carried it through a jacketed water-cooled feeder tube into the bubbling fluidized bed reactor. The pyrolysis temperature was maintained between 425 °C and 550 °C, and the apparent pyrolysis vapor residence time was less than 2.90 s depending on reaction conditions. Thus, the reaction of in a bubbling fluidized bed reactor is a fast pyrolysis considering residence time of pyrolysis vapor. The system was turned on 2 h before experiment, and the setting value of reaction temperature was constant within ±10 °C. The experiments lasted from 1 h to 2 h after 1 h stabilization period before *Milkweed* feeding, and the feed rate of sample was between 100 g/h and 200 g/h. The feed rate of sample, gas flow rate and reactor temperature were kept constant during each run. The sand bed and the reactor temperature were measured and controlled by three K-type thermocouples inserted into a thermal well in the bubbling fluidized bed reactor.

The pyrolysis vapor (>425 °C) exiting the reactor was condensed in a series of two ethylene glycol-cooled condensers and an electrostatic precipitation (ESP) unit. The aqueous phase (water) was condensed in the ethylene glycol-cooled condenser which was maintained below −10 °C. The aerosol, which was not condensed

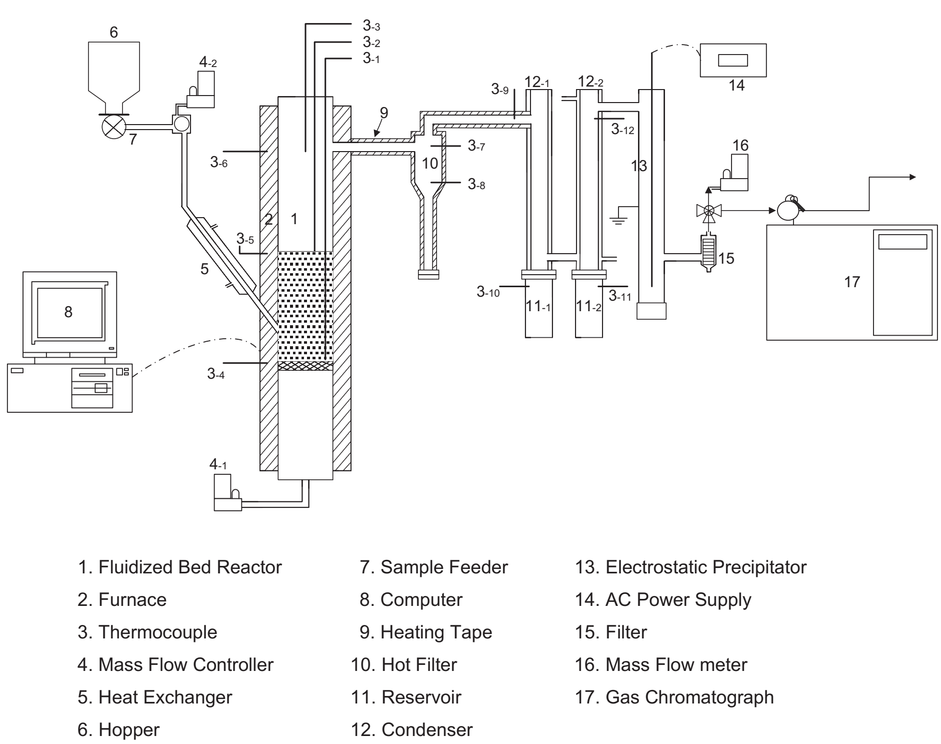

Fig. 1. Schematic diagram of bubbling fluidized bed reactor.

in the ethylene glycol/water-cooled condenser, was collected in the ESP unit. The char fraction was separated in hot gas filter. Solid, liquid and gas yields were determined gravimetrically by weighting the apparatus before and after each experiment. The gas yield was calculated by difference: Gas yield = 100 – (Char/Ash) yield – Total Liquid yield. The non-condensable gases were connected to SRI 8610C gas chromatograph (SRI Instruments, Torrance, CA) for online analysis. The GC was equipped with FID and TCD; Molecular sieve 13× was used to analyze C_1–C_6 hydrocarbons, and Hysep D column was used to analyzed hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). The pH of aqueous phase was measured using Mettler Toledo pH Meter and probe (Mettler-Toledo GmbH, Switzerland). The ^{1}H and ^{13}C NMR spectra of bio-oil were recorded on a JEOL 300 MHz NMR spectrometer (JEOL, Ltd., Tokyo, Japan). Bio-oil (0.2 g) was dissolved in 0.3 ml deuterated dimethyl sulfoxide-d_6 (DMSO-d_6) in a 5 mm sample tube. The observing frequency for the ^{13}C nucleus, the pulse width, the acquisition time, and the relaxation delay were 100.58 MHz, 10 μs, 1.58 s, and 2 s, respectively. The spectra were obtained with 3000 scans and a sweep width of 20 kHz.

3. Results and discussion

3.1. Characteristics of Milkweed

The volatile matter and the fixed carbon content of *Milkweed* were 79.15 wt% and 13.48 wt%, respectively. The moisture and ash contents and HHV of *Milkweed* were 7.58 wt%, 11.20 wt%, and 16.67 MJ/kg, respectively. The elements of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) were 41.92 wt%, 6.0 wt%, 2.97 wt% and 49.11 wt%, respectively. The H/C molar ratio of *Milkweed* was 1.72 and the O/C ratio was 0.88 compared to 1.53 and 0.70, respectively, reported for Pinyon pine wood by Kim et al. (2014). The HHV is strongly dependent on the carbon, oxygen, and ash contents of the feedstock; high carbon as well as low oxygen and ash results in high HHV. The HHV of *Milkweed* was 16.67 MJ/kg compared to 18.60 MJ/kg reported for *Pinyon* pine because of the higher O/C ratio and higher ash content of this feedstock.

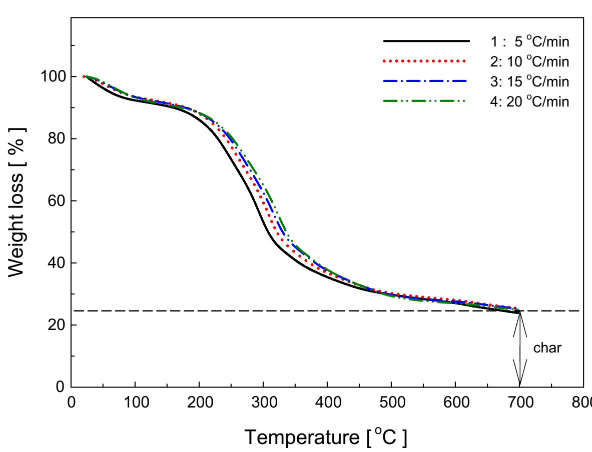

Fig. 2. Weight loss curves for *Milkweed* at heating rates of 5, 10, 15, and 20 °C/min.

3.2. Thermogravimetric analysis and kinetic parameters for Milkweed

Fig. 2 shows TGA percent weight loss of *Milkweed* in N_2 atmosphere at four different heating rates 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The reaction of *Milkweed* in TGA is a slow pyrolysis although the heating rate are varied from 5 °C/min to 20 °C/min under 700 °C. Average char yield of *Milkweed* was 24.96 wt% compared to 20.0 wt% reported for Pinyon pine (Kim et al. (2014)), which is found in western United States, is a 10–30 foot tall tree, growing in the pinyon-juniper woodlands (Short et al., 1997). The high char yield in *Milkweed* pyrolysis was attributed to the high ash content (11.2–11.7 wt%) of the feedstock. Ash content of *Pinyon* pine was 0.44 wt%, and char yield of that material was lower than *Milkweed*. Kim et al. (2013) reported pyrolysis characteristics and kinetics of macro algae (*Sagarssum* sp.); the average char content was 46.17 wt% from the TGA heating rate of 5–20 °C/min. Thus, the higher char yield from the pyrolysis of biomass is attributed to the high inorganic materials, which is characterized as ash (11.20 wt%) as shown in Table 1.

The results of thermogravimetric experiments were expressed as a function of conversion *X*, as defined in Eq. (1).

$$X = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

where, W_0 is the initial mass of sample; W is the mass of pyrolyzed sample; W_∞ is the final residual mass.

The degree of conversion versus temperature for *Milkweed* in nitrogen atmosphere is shown in Fig. 2, and the thermogravimetric characteristics showed similar patterns at the heating rates of 5, 10, 15, and 20 °C/min. The weight loss below 120 °C was attributed to desorption of moisture bound to the surface and pores of *Milkweed* samples. The TGA curves of the *Milkweed* samples showed major decomposition occurring between 200 °C and 500 °C. The maximum weight loss temperature was 296 °C at the heating rate of 5 °C/min. Gu et al. (1992) reported thermal characterization of *Milkweed floss* at nitrogen flow 100 ml/min with heating rate of 5 °C/min. The weight loss was 71 wt% between 100 °C and 350 °C, and 11 wt% between 350 °C and 600 °C and the maximum degradation temperature was 315 °C. When lignocellulosic biomass are pyrolyzed, hemicellulose starts to decompose around 290 °C, and cellulose decomposes over 30 °C range between 320 °C and 380 °C (Wang et al., 2008). Lignin has a broad decomposition temperature range between 200 °C and 500 °C which makes it impossible to define an activation energy for the reaction (Guar and Reed, 1994; Vamvuka et al., 2003; Alvarez and Vázquez, 2004). The differential thermogram of *Milkweed* (Fig. 3) showed four major peaks between 200 °C and 500 °C. The first peak for the *Milkweed* was a small left shoulder at 230–280 °C for the heating rate of 5 °C/min, which was attributed to the

Table 1
Calculated kinetic parameters for the pyrolysis of *Milkweed.*

Ea (kJ/mol)		Conversion (%)										
		5 70.22	10 72.78	20 144.65	30 142.81	40 152.70	50 146.60	60 152.50	70 181.79	80 257.63	85 302.03	90 752.35
n	0th	2.25×10^{7}	6.09×10^{5}	8.36×10^{11}	1.23×10^{11}	2.91×10^{11}	2.82×10^{10}	4.48×10^{10}	3.17×10^{12}	1.95×10^{17}	3.85×10^{19}	3.45×10^{50}
	1st	2.37×10^{7}	6.77×10^{5}	1.04×10^{12}	1.76×10^{11}	4.84×10^{11}	6.64×10^{10}	1.12×10^{11}	1.05×10^{13}	9.74×10^{17}	2.57×10^{20}	3.45×10^{51}
	2nd	2.50×10^{7}	7.52×10^{5}	1.31×10^{12}	2.51×10^{11}	8.07×10^{11}	1.13×10^{11}	2.80×10^{11}	3.52×10^{12}	4.87×10^{18}	1.71×10^{21}	3.45×10^{52}

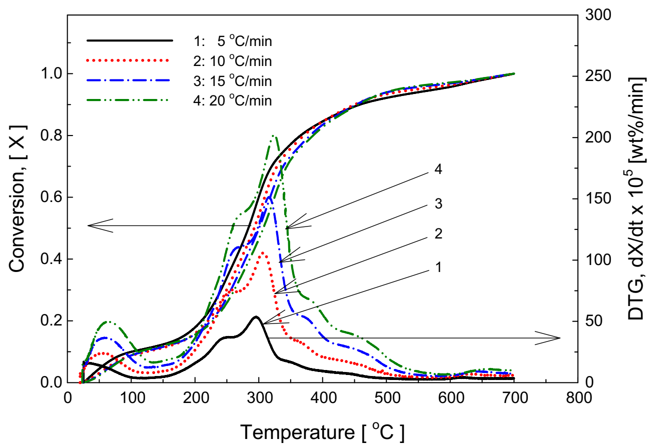

Fig. 3. Thermogravimetric and differential thermogravimetric curves of *Milkweed* in nitrogen atmosphere at heating rate of 5, 10, 15 and 20 °C/min.

decomposition of hemicelluloses, while the main peak at 296 °C was due to the decomposition of cellulose, which is similar to the results of other researchers (Guar and Reed, 1994; Alvarez and Vázquez, 2004). It is known that *Milkweed* contains latex, but the concentrations of latex vary and are too low for commercial exploitation. There is a small peak between 330 °C and 380 °C, which appears to be due to the decomposition of latex in *Milkweed*. Seidelt et al. (2006) reported that natural rubber decomposed between 330 °C and 390 °C at 5 K/min, which supports the interpretation of the above thermogram for the *Milkweed*. Lignin does not decompose at a clearly defined temperature, but decomposes across a wide range of temperature (210–500 °C). It is, therefore plausible that the peak between 400 °C and 500 °C is due to the decomposition of lignin.

The TGA graphs were analyzed using the differential method to obtain the pyrolysis kinetic parameters from the thermogravimetric data (Friedman, 1963; Liou et al., 1997; Kim and Agblevor, 2007). The rate of conversion, dX/dt, during the pyrolysis was expressed as below.

$$\ln\left(\frac{dX}{dt}\right) = \ln[A\cdot(1-X)^n] - \frac{E}{R}\cdot\frac{1}{T} \tag{2}$$

where E, k, R, t, and T activation energy (kJ/mol), pyrolysis rate constant (s^{-1}), gas constant (J/mol K), pyrolysis time (min), and pyrolysis temperature (K), respectively. The apparent energy of activation E, from Eq. (2), can be determined from the relationship between $\ln(dX/dt)$ and $1/T$ if $\ln[A{\cdot}(1-X)^n]$ is constant. The intercept $(\ln(A{\cdot}(1-X)^n)$ in Eq. (2) can be calculated at each conversion. Since the intercept varies with the degree of conversion, Eq. (3), a plot of $\ln(1-X)$ vs intercept at each conversion can be used to determine the pre-exponential factor (A) when the apparent order of reaction (n) is assumed to be 0, 1 or 2.

$$\ln A + n\cdot\ln(1-X) = K \tag{3}$$

where K = intercept at each conversion X

The variations of apparent activation energies as a function of conversion for *Milkweed* pyrolysis is shown in Table 1. The range of apparent activation energies of *Milkweed* was between 70.22 kJ/mol and 752.35 kJ/mol in nitrogen atmosphere for conversions between 5% and 90%. The moisture on the surfaces of *Milkweed* sample vaporized below 120 °C, as seen in DGT curves in Fig. 2. It was assumed that the activation energy of 70.22 kJ/mol and 72.78 kJ/mol at 5% and 10% conversion corresponded to the vaporization of moisture. The apparent activation energies were similar to the conversion between 20% and 60%. As shown in the TG curves, hemicellulose and cellulose decomposed below 60% conversion and the corresponding activation energy was between 144.65 kJ/mol and 152.50 kJ/mol. When the temperature was between 330 °C and 380 °C which corresponded to 70–80% conversions, the apparent activation energies were 181.79–257.63 kJ/mol which is similar to the apparent activation energy (254 kJ/mol) reported by Seidelt et al. (2006) for natural rubber. The DTG had a shoulder above 400 °C, which tailed and continued at a relatively slower rate probably because of the deposition of char on the undecomposed lignin. The pre-exponential factor was between 10^{10} and 10^{17} min^{-1} when the *Milkweed* conversion was between 20% and 80%, but then increased rapidly, probably because of further devolatilization of the residual char.

3.3. Product yield and characteristics

Table 2 shows the effect of reaction temperature on product yields of total liquid (organics and water), char, and gas from the pyrolysis of *Milkweed* in a bubbling fluidized bed reactor. Analysis of char/coke, condensable product and non-condensable gaseous product was explained in Section 2 in detail.

The reaction temperature for the fast pyrolysis of *Milkweed* in a bubbling fluidized bed was determined from the TG and DTG curves in Fig. 3. When the reaction temperature reached 425 °C, the average conversion was 86.92% at each heating rate. It was assumed that most of hemicellulose, cellulose and natural rubber had decomposed between 425 °C and 550 °C for the fast pyrolysis. As the pyrolysis temperature was increased from 425 °C to 550 °C, total liquid yield ranged from 40.74 wt% to 44.19 wt%. However, bio-oil (organics) fraction slightly decreased with increasing temperature but water fraction did not much change. Char/coke yields were similar for different temperatures, whereas the gas yield increased with increasing reaction temperature. Total liquid yield was highest (44.19 wt%) at 425 °C, and gas yield was highest (33.33 wt%) at 550 °C. *Milkweed* had high ash content (11.20 wt%) compared to most woody biomass, but its char/coke yield at 475 °C was 24.5 wt% which is similar to that for Pinyon-juniper wood reported by Yathavan and Agblevor (2013). The relatively low char/coke yield for *Milkweed* was rather surprising because ash is supposed to be a major promoter of char/coke formation. Inorganic materials in ash such as potassium (K), calcium (Ca) and phosphorous (P) are known to catalyze char formation reactions (DeGroot and Shafizadeh, 1984). High char/coke yield (33.84–44.71 wt%) was reported (Kim et al., 2009) for the fast pyrolysis of chicken litter which had high ash content (21.45–22.80 wt%). Therefore, high char/coke formations were expected from *Milkweed* pyrolysis because of its high ash content, but surprisingly the *Milkweed* and *Pinyon-Juniper* had similar char/coke yields. The relatively low char/coke yield from the *Milkweed* could be probably due to the latex content of the biomass whose decomposition products did not further react with the inorganic species to form char/coke.

The elemental analysis and HHV of bio-oil from *Milkweed* are shown in Table 2. The carbon (C) contents of the bio-oils were 25 wt% higher than that of *Milkweed* feedstock, but the oxygen (O) contents were 32 wt% less than that of *Milkweed* feedstock. The nitrogen was significantly concentrated in the bio-oil, especially, bio-oil obtained at 450 °C showed the highest nitrogen content, which was 2.22 times higher than *Milkweed* sample. Higher heating value (HHV) is directly dependent on the carbon and hydrogen contents of the feedstock and inversely with oxygen content. HHV of *Milkweed* bio-oil was between 30.33 MJ/kg and 32.04 MJ/kg, which were much higher than the HHVs of most lignocellulosic biomass pyrolyzed under similar conditions. Agblevor et al. (1995) researched fast pyrolysis of stored woody and herbaceous biomass feedstocks and the HHV of bio-oil from

Table 2
Effect of reaction temperature on product yields in a bubbling fluidized bed for *Milkweed*; feeding rate = 200 g/h.

		Temperature (°C)					
		425 °C	450 °C	475 °C	500 °C	525 °C	550 °C
Product yield (wt%)	Total liquid	44.19	42.86	42.24	42.02	43.33	40.74
	Organics	26.35	22.99	23.96	23.74	24.19	21.96
	Water	17.84	19.87	18.28	18.29	19.14	18.78
	Char	27.91	28.04	24.84	26.06	25.56	25.93
	Gas	27.90	29.10	32.92	31.92	31.11	33.33
Elemental analysis of bio-oil (wt%)	C	69.07 ±0.90	67.34 ±0.56	69.07 ±0.36	70.79 ±0.40	70.74 ±0.92	67.88 ±0.75
	H	8.81 ±0.22	8.64 ±0.03	8.97 ±0.15	8.90 ±0.08	8.99 ±0.11	9.01 ±0.14
	N	5.52 ±0.52	6.60 ±0.30	5.67 ±0.23	6.17 ±0.14	6.34 ±0.50	6.44 ±0.05
	O	16.60	17.42	16.29	14.14	14.33	16.67
HHV of bio-oil (MJ/kg)		31.28	30.33	30.92	32.09	32.24	31.27
pH of aqueous phase		6.90 ±0.04	7.69 ±0.02	7.37 ±0.01	7.76 ±0.02	7.47 ±0.02	7.71 ±0.02
Gas selectivity (mol%)	CO	20.04	20.79	21.99	20.52	23.65	16.77
	CO_2	71.03	68.67	72.58	69.07	53.44	51.08
	H_2	0.00	0.00	0.00	0.00	10.63	21.45
	CH_4	4.73	5.68	2.07	5.37	7.14	7.33
	C_2H_6	0.64	0.74	0.26	0.57	0.78	0.45
	C_3H_8	1.22	1.27	1.38	1.76	1.11	0.62
	$>C_4$ hydrocarbons	2.35	2.75	1.72	2.71	3.25	2.31

fresh and stored biomass feedstocks were between 22.5 MJ/kg and 24.7 MJ/kg. In their study, they observed that HHV of bio-oils decreased slightly with storage time for all the feedstock. The HHV of bio-oil was 24.87 MJ/kg for the fast pyrolysis of *Pinyon-Juniper* using sand pyrolysis medium, whereas the HHVs increased to 28.55 MJ/kg and 29.46 MJ/kg, respectively, when Yathavan and Agblevor (2013) used HZSM-5 and red mud as a catalytic pyrolysis medium. Mante et al. (2012) researched the influence of recycling non-condensable gases (NCG) on the fractional catalytic pyrolysis of hybrid poplar at 470 °C. They reported recycling of NCG increased the HHV and the pH of the bio-oil. The maximum HHV was 31.27 MJ/kg in the NCG recycle run with FCC/FeCrCu/CoMo catalyst, and the improvement of bio-oil quality were attributed to the enhanced cracking and deoxygenation reactions such as decarboxylation, decarbonylation and demethoxylation. The ratios of H/C of bio-oil from *Milkweed* were between 0.96 and 1.18, and those of O/C were between 0.15 and 0.18. The ratio of O/C of bio-oil decreased drastically compared to raw *Milkweed* feedstock (0.88). In terms of energy density of bio-oil, *Milkweed* is a very promising renewable resource.

The pH of most lignocellulosic bio-oil is usually less than 4 for both catalytic and non-catalytic pyrolysis products (Yathavan and Agblevor, 2013; Mante et al., 2012; Bridgwater, 2012). The ethylene glycol/water-cooled condensate was a two phase product containing organic compounds and water from the 1st condenser (Fig. 1). The pH of the aqueous phase was almost neutral (6.90–7.71), which is the highest reported for any lignocellulosic raw bio-oil and suggests that bio-oil from *Milkweed* fast pyrolysis may be less corrosive than most lignocellulosic bio-oils.

The gas products CO, CO_2 and CH_4 were similar for all reaction temperatures, but the concentration of gas components varied with pyrolysis temperature. The CO_2 contents were highest for all reaction temperatures, but was similar to the results of Yathavan and Agblevor (2013). The concentration of CO_2 decreased with increasing reaction temperature, whereas CH_4 increased. The pyrolysis behavior of biomass by means of TGA-MS has been studied for lignocellulosic biomass and marine biomass (Sanchez-Silva et al., 2012). Hydrogen production was only observed at temperatures higher than 500 °C. The production of H_2 at 525 °C and 550 °C in the fast pyrolysis of *Milkweed* were similar to those reported in literature.

The product distributions under different feeding rates and reaction temperature are shown in Table 3. Total liquid yield increased with increasing feeding rates and temperature, but there was no obvious effect of feeding rates on char/coke and gas yields. A fluidized bed is known to separate into 2 beds such dense and suspension due to the segregation effect (Luo et al., 2005; Heo et al., 2010). The temperature of dense bed is higher than that of suspension bed at higher feeding rates, which could enhance gas flow velocity, and it could prevent secondary cracking of pyrolysis vapors in fluidized bed and result in increased total liquid yield (Luo et al., 2004; Heo et al., 2010). Total liquid yield, especially organic fraction, increased with increasing feeding rates of *Milkweed* sample, which was in good agreement with reported results. The elemental composition, HHV and pH data did not showed any obvious influence of feeding except for a slight decrease in oxygen content with increased feeding rate. The gaseous products were affected by the feeding rate of the *Milkweed* biomass; higher feeding rates at 475 °C led to increase in CO production while CO_2 decreased. CO_2 was mostly produced from carboxyl release at a relatively low temperature and low feeding rate (Luo et al., 2004; Bulushev and Ross, 2011). In this work, H_2 was observed at 200 g/h feeding rate, which could be due to secondary reaction of volatiles that released CO and H_2.

Table 4 shows the effect of fluidization velocity on product distribution. Long vapor residence time caused secondary reaction of primary products such as thermal cracking, repolymerization, and recondensation, resulting in decreasing yields of specific products such as organic liquid fraction. Effect of vapor residence time on product distributions was carried out at 2.0 U_{mf}, 3.0 U_{mf}, and 4.0 U_{mf} at 425 °C which corresponded to residence time 2.90 s, 1.93 s, and 1.45 s, respectively. Total liquid yields as well as organic fraction were highest at 3.0 U_{mf}, whereas gas yield was low. There was no obvious influence of fluidization velocity on elemental composition and HHV. The pH of aqueous phase decreased with increasing fluidization velocity, and methane and $>C_4$ hydrocarbons also decreased with increasing fluidization velocity.

Table 3
Effect of feeding rate on product yields in a bubbling fluidized bed for *Milkweed*.

		Reaction conditions					
		425 °C			475 °C		
		100 g/h	150 g/h	200 g/h	100 g/h	150 g/h	200 g/h
Product yield (wt%)	Total liquid	41.97	44.94	44.19	39.90	41.75	42.24
	Organics	23.59	25.26	26.35	21.80	22.15	23.96
	Water	18.38	19.68	17.84	18.10	19.60	18.28
	Char	27.98	30.34	27.91	26.26	26.70	24.84
	Gas	30.05	24.72	27.90	33.84	31.56	32.92
Elemental analysis of bio-oil (wt%)	C	66.59 ±1.02	66.57 ±0.40	69.07 ±0.90	69.05 ±0.52	68.64 ±0.68	69.07 ±0.36
	H	8.90 ±0.30	8.83 ±0.10	8.81 ±0.22	8.72 ±0.11	8.95 ±0.14	8.97 ±0.15
	N	4.36 ±0.10	4.75 ±0.07	5.52 ±0.52	5.04 ±0.12	4.66 ±0.04	5.67 ±0.23
	O	20.15	19.85	16.60	17.19	17.75	16.29
HHV of bio-oil (MJ/kg)		31.96	31.94	31.28	32.87	32.58	30.92
pH of aqueous phase		7.35 ±0.02	6.75 ±0.06	6.90 ±0.04	7.38 ±0.01	7.41 ±0.03	7.37 ±0.01
Gas selectivity (mol%)	CO	19.95	22.39	20.04	19.91	18.06	32.21
	CO_2	76.04	70.41	71.03	68.93	74.37	49.83
	H_2	0.00	0.00	0.00	0.00	0.00	6.84
	CH_4	2.13	3.68	4.73	7.16	4.15	6.01
	C_2H_6	0.25	0.46	0.64	0.51	0.35	0.65
	C_3H_8	1.00	1.15	1.22	1.02	0.92	1.32
	>C_4 hydrocarbons	0.63	1.92	2.35	2.48	2.16	3.14

Table 4
Effect of fluidization velocity on product yields in a bubbling fluidized bed for Milkweed: 425 °C, 150 g/h.

		Fluidization velocity, U_{mf}		
		$2.0 \times U_{mf}$	$3.0 \times U_{mf}$	$4.0 \times U_{mf}$
Product yield (wt%)	Total liquid	42.41	44.94	42.11
	Organics	22.51	25.26	23.83
	Water	19.90	19.68	18.28
	Char	26.70	30.34	27.92
	Gas	30.89	24.72	29.95
Elemental analysis of bio-oil (wt%)	C	65.11 ± 0.63	66.57 ± 0.40	69.05 ± 0.52
	H	8.57 ± 0.18	8.84 ± 0.10	8.72 ± 0.11
	N	4.77 ± 0.14	4.75 ± 0.07	5.04 ± 0.12
	O	21.55	19.85	17.19
HHV of bio-oil (MJ/kg)		32.52	31.94	32.33
pH of aqueous phase		7.15 ± 0.03	6.75 ± 0.05	6.64 ± 0.02
Gas selectivity (mol%)	CO	20.38	22.39	20.64
	CO_2	71.65	70.41	72.64
	H_2	0.00	0.00	0.00
	CH_4	4.19	3.68	3.50
	C_2H_6	0.45	0.46	0.47
	C_3H_8	1.10	1.15	1.08
	>C_4 hydrocarbons	2.23	1.92	1.85

U_{mf} : Minimum fluidization velocity.

3.4. Bio-oil analysis

Bio-oil, which was collected in ESP, was used for the ^{1}H NMR and ^{13}C NMR analysis. From the spectra on the ^{1}H NMR, it is evident that there are major differences in the overall chemical makeup of the bio-oils from the different reaction temperatures. The region between 0.5 ppm and 1.5 ppm represents alkane protons, which showed the highest relative concentration. The peak height was lower at 475 °C than those at 425 °C and 525 °C. The region from 1.5 ppm to 3.0 ppm which also represent protons on aliphatic carbon atoms was lower at 475 °C than those of 425 °C and 525 °C like alkanes proton. The region, from 3.0 ppm 4.4 ppm, are the protons of alcohols and amines, and the region between 4.4 ppm and 6.0 ppm are methoxy, carbohydrates, and phenolic-OH, alkanes and aliphatic protons. The peaks in these regions were most intense at 475 °C. This means that reaction pathways are different at 475 °C to 425 °C and 525 °C. Mullen et al. (2013) used ^{1}H and ^{13}C NMR to characterize fast pyrolysis bio-oils from protein-rich *pennycress* seed cake. Their results showed high alkane and methoxy protons similar to those observed in the *Milkweed* bio-oil. The aromatic region of the spectrum (6.0–8.5 ppm) showed relatively lower peak at 475 °C compared to those at 425 °C and 525 °C. This region contains not only those hydrogen atoms in benzenoids, but also those in heteroaromatics containing O and N (Mullen et al., 2009). From the elemental analysis of bio-oils (Tables 3 and 4), the content of N in bio-oils was between 4.36 wt% and 6.44 wt%. Thus, it was assumed that most of N compounds in of *Milkweed* existed as heteroaromatics and amines. The pH for the mustard family pyrolysis oils was measured at 6.5–8.0 (Boateng et al., 2010). They explained the high pH of those bio-oils was due to their high organic nitrogen content (4–11 wt%) in the liquids. From GC/MS analysis, nitrogen was contained in cyclic amines (pyridines, pyrroles, indoles, piperidines, and their derivatives), which effected neutralizing the organic acids such as formic acid, acetic acid, propanoic acid, and others. The nitrogen content in bio-oils for *Milkweed* was between 4.36 wt% and 6.60 wt% depending on reaction conditions. The high pH of *Milkweed's* bio-oils was similar to those of pennycress press cake pyrolysis oil.

The major differences of ^{13}C NMR spectra between 425 °C bio-oil and 475 °C bio-oil appeared in the region from 0 ppm to 55 ppm. This region represents aliphatic hydrocarbons which corroborates the proton NMR data. Bio-oils from lignocellulosic biomass showed higher contents of levoglucosan, anhydrosugars, alcohols, ethers (60–105 ppm) and C=O groups (160–180 ppm) than bio-oil from *Milkweed* (Mullen et al., 2009; Agblevor et al., 2010; Yathavan and Agblevor, 2013). In ^{13}C NMR spectra of *Milkweed* pyrolysis oil, the aliphatic hydrocarbons and aromatic hydrocarbons signals were higher than other groups. HHVs of bio-oil from *Milkweed* samples at different reaction conditions

were over 30 MJ/kg (Tables 2–4) for non-catalytic fast pyrolysis. Thus, it appears that higher HHV of bio-oil from *Milkweed* was because of the higher aliphatic and aromatic hydrocarbon content.

The studies clearly demonstrate that *Milkweed* pyrolysis liquids and gases have higher energy density than those from most lignocellulosic biomass feedstocks. The high pH of these oils also make them superior products. Thus *Milkweed* which can be harvested about three times a year can potentially out perform traditional feedstocks like *switchgrass*, *miscanthus* and *hybrid poplar* wood both in feedstocks yield and energy density. The only potential disadvantage of this feedstock is the high nitrogen content of the bio-oil.

4. Conclusions

Unlike most lignocellulosic biomass pyrolysis oils, the *Milkweed* pyrolysis oil had very high HHV (>30 MJ/kg) and very high pH. The ^{13}C NMR analysis of the pyrolysis oil showed a large fraction of aromatic and aliphatic hydrocarbons, therefore could be easily upgraded to hydrocarbon fuels. The *Milkweed* feedstock appear to be potentially superior to most lignocellulosic biomass feedstocks in terms of high energy density and it could be harvested about three times per year. It could be cultivated on a large scale without competing with food supply and it could potentially outcompete traditional bioenergy feedstocks such switchgrass and hybrid polar.

Acknowledgements

Utah Science and Technology Research (USTAR) Program and LG Yonam Culture Foundation are acknowledged for their financial support of this project.

References

Agblevor, F.A., Besier, S., Wiselogel, A.E., 1995. Fast pyrolysis of stored biomass feedstocks. Energy Fuels 9, 635–640.
Agblevor, F.A., Beis, S., Mante, O., Abdoulmoumine, N., 2010. Fractional catalytic pyrolysis of hybrid poplar wood. Ind. Eng. Chem. Res. 49, 3533–3538.
Alvarez, V.A., Vázquez, A., 2004. Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposite. Polym. Degrad. Stab. 84, 13–21.
Bridgwater, A.V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis of biomass. Org. Geochem. 30, 1479–1493.
Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 38, 68–94.
Boateng, A.A., Mullen, C.A., Goldberg, N.M., 2010. Producing stable pyrolysis liquids from the oil-seed presscakes of mustard family plant: *Pennycress* (*Thlaspi arvense* L.) and *Camelina* (*Camelina sativa*). Energy Fuels 24, 6624–6632.
Bulushev, D.A., Ross, J.R.H., 2011. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. Catal. Today 171, 1–13.
Choi, G.-H., Kim, S.-S., Kim, J., Joo, D.-S., Lee, J., 2011. Pyrolysis characteristics of Hemp by-products (stem, root and blast). Appl. Chem. Eng. 22, 508–513.
DeGroot, W.F., Shafizadeh, F., 1984. The influence of exchangeable cations on the carbonization of biomass. J. Anal. Appl. Pyrol. 6, 217–232.
Evangelista, R.L., 2007. Milkweed seed wing removal to improve oil extraction. Ind. Crops Prod. 25, 210–217.
Foster, K.E., Karpiscak, M.M., 1983. Arid land plants for fuel. Biomass 3, 269–285.
Friedman, H.L., 1963. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J. Polym. Sci. 6, 183–195.
Gu, P., Hessley, R.K., Pan, W.-P., 1992. Thermal characterization analysis of milkweed floss. J. Anal. Appl. Pyrol. 24, 147–161.
Guar, S., Reed, T.B., 1994. An Atlas of Thermal Data for Biomass and Other Fuels. National Renewable Energy Laboratory.
Heo, H.S., Park, H.J., Dong, J.-I., Park, S.H., Kim, S., Suh, D.J., Suh, Y.-W., Kim, S.-S., Park, Y.-K., 2010. Fast pyrolysis of rice husk under different reaction conditions. J. Ind. Eng. Chem. 16, 27–31.
Kim, S.-S., Agblevor, F.A., 2007. Pyrolysis characteristics and kinetics of chicken litter. Waste Manage. 27, 135–140.
Kim, S.-S., Agblevor, F.A., Lim, J., 2009. Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. J. Ind. Eng. Chem. 15, 247–252.
Kim, S.-S., Ly, H.V., Kim, J., Choi, J.H., Woo, H.C., 2013. Thermogravimetric characteristics and pyrolysis kinetics of Alga *Sagarssum* sp. biomass. Bioresour. Technol. 139, 242–248.
Kim, S.-S., Shenoy, A., Agblevor, F.A., 2014. Thermogravimetric and kinetic study of Pinyon pine in the various gases. Bioresour. Technol. 156, 297–302.
Liou, T.-H., Chang, F.-W., Lo, J.-J., 1997. Pyrolysis kinetics of acid-leached rice husk. Ind. Eng. Chem. Res. 36, 568–573.
Luo, Z., Wang, S., Liao, Y., Zhou, J., Gu, Y., Cen, K., 2004. Research of biomass fast pyrolysis for liquid fuel. Biomass Bioenergy 26, 455–462.
Luo, Z., Wang, S., Cen, K., 2005. A model of wood flash pyrolysis in fluidized bed reactor. Renewable Energy 30, 377–392.
Mante, O.D., Agblevor, F.A., 2010. Influence of pine wood shavings on the pyrolysis of poultry litter. Waste Manage. 30, 2537–2547.
Mante, O.D., Agblevor, F.A., Oyama, S.T., McChung, R., 2012. The influence of recycling non-condensable gases in the fractional catalytic pyrolysis of biomass. Bioresour. Technol. 111, 482–490.
Mullen, C.A., Strahan, G.D., Boateng, A.A., 2009. Characterization of various fast-pyrolysis bio-oils by NMR spectroscopy. Energy Fuels 23, 2707–2718.
Mullen, C.A., Boateng, A.A., Reichenbach, S.E., 2013. Hydrotreating of fast pyrolysis oils from pretein-rich pennycress seed cake. Fuel 111, 797–804.
Sanchez-Silva, L., Lopez-Gonzalez, D., Villasenor, J., Sanchez, P., Valverde, J.L., 2012. Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. Bioresour. Technol. 109, 163–172.
Seidelt, S., Muiller-Hagedorn, M., Bockhorn, H., 2006. Description of tire pyrolysis by thermal degradation behavior of main components. J. Anal. Appl. Pyrolysis 75, 11–18.
Short, H.L., Evans, W., Boeker, E.L., 1997. The use of natural and modified Pinyon pine-juniper woodlands by deer and elk. J. Wildlife Manage. 41, 543–559.
Wang, G., Li, W., Li, B., Chen, H., 2008. TG study on pyrolysis of biomass and its three components under syngas. Fuel 87, 552–558.
Vamvuka, D., Kakaras, E., Kastanaki, E., Grammelis, P., 2003. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel 82, 1949–1960.
Yathavan, B., Agblevor, F.A., 2013. Catalytic pyrolysis of Pinyon-Juniper using Red Mud and HZSM-5. Energy Fuels 27, 6858–6865.